

I.
Measurement of Decomposition Potentials

II.
Transfer Resistance

A Thesis
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

By
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A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

THE MEASUREMENT OF DECOMPOSITION POTENTIALS.¹

By ALFRED L. FERGUSON² and GERRIT VAN ZYL.³

ABSTRACT.

In this investigation an apparatus is developed, by which a direct comparison is made between all the values obtained by the commutator and direct methods for measuring decomposition potential and overvoltages. Evidence is given which should help materially to settle the controversy, which has so long existed concerning the relative merits of these two methods. All measurements made by the commutator method are averages, and depend to a large extent upon the operation and mechanical construction of the commutator.

Two methods have been employed extensively for the determination of decomposition potentials and overvoltages. The first, called the direct method, was suggested by Fuchs³ in 1875, and was later used by Caspari,⁴ Coehn and Dannenberg,⁵ Möller,⁶ and many other investigators. The second, or commutator method, in which a rotating commutator is used, was suggested by LeBlanc⁷ and later used by Pring⁸ and others, but especially by Newbery.⁹

Opinions differ as to which of the two methods of measurement gives true overvoltage values. J. M. Pring states that the

¹ Manuscript received February 15, 1924. The work herein reported is a portion of the thesis presented by Gerrit Van Zyl to the faculty of the graduate school of the University of Michigan in part fulfillment of the requirements for the degree of Doctor of Philosophy.

² Chemical Laboratory, Univ. of Michigan, Ann Arbor, Mich.

³ Pogg. Ann., 156, 158 (1875).

⁴ Z. phys. Chem., 30, 89 (1899).

⁵ Z. phys. Chem., 38, 609 (1901).

⁶ Z. phys. Chem., 65, 226 (1909).

⁷ Z. phys. Chem., 5, 469 (1890).

⁸ Pring and Tainton, J. Chem. Soc., 105, 712 (1914); Pring, Z. Elektrochemie, 19, 255 (1913).

⁹ J. Chem. Soc., 105, 2419 (1914); Man. Men. Lit. and Philo. Soc., 60, No. 11 (1916), also 61, No. 9 (1917).

disadvantage of the direct method is that the values contain not only the polarization potential, but also the additional potential which is due to the "transfer resistance" between the electrode and electrolyte during the passage of the current. He favors the commutator method, since in his opinion it gives the true value for polarization potential or "back e. m. f."

Newbery maintains that the direct method gives true overvoltage values only at extremely low current densities, while at high current densities the values obtained are erroneous, because the potential necessary to overcome the resistance of a film of gas around the electrode is included in the measurements. The work of MacInnes and Adler,¹⁰ and MacInnes and Contieri¹¹ on hydrogen overvoltage, in which they use the direct method with slight modification, is severely criticised by Newbery¹². W. R. Mott¹³ states that the use of a rotating commutator often introduces errors due to capacity effects. Bennett and Thompson,¹⁴ in their discussion of overvoltage, consider only values obtained by means of the commutator method. Chaney¹⁵ criticises Bennett because he calls overvoltage, as he defines it, "true overvoltage," and overvoltage phenomena which arise from resistance and capacity effect, "false overvoltage."

A point which deserves special mention is that the discharge potential has usually been measured too soon (in some cases only half a minute) after the charging potential was applied or increased. Another question is the proper rate of rotation of the commutator. LeBlanc¹⁶ used a commutator rotating at the rate of 1200 to 1500 r. p. m. Newbery states that when the rate of rotation is 1000 r. p. m., or more, there is no change in the overvoltage, and that the fall of discharge potential in 1/2000 of a minute is negligibly small.

From an analysis of the existing literature on decomposition potentials the authors felt convinced that both methods contained so many elements of uncertainty, and that the subject of overvoltage measurement is so indefinite that an intensive study of

¹⁰ J. Am. Chem. Soc., **41**, 194 (1919).

¹¹ J. Am. Chem. Soc., **41**, 2013 (1919).

¹² J. Am. Chem. Soc., **42**, 2007 (1920).

¹³ Trans. Am. Electrochem. Soc., **29**, 181 (1916).

¹⁴ Trans. Am. Electrochem. Soc., **29**, 269 (1916).

¹⁵ Trans. Am. Electrochem. Soc., **29**, 181 (1916).

¹⁶ Z. phys. Chem., **5**, 469 (1890).

the whole question was essential before it could be considered a reliable method of electrochemical investigation. They were inclined to ask the same question which MacInnes did in his article, why should there be any difference between the values obtained by the two methods? An answer to this question should settle the controversy concerning the use of these methods.

The first task was to develop a set-up which would permit measurements whereby all of the various questionable features in connection with decomposition potential measurements could be accurately studied. Such a set-up must permit measurements to be made by both methods at the same time and under identically the same conditions.

APPARATUS AND METHOD.

The apparatus as finally arranged is shown in Fig. 1. The charging circuit consists of a storage battery BA' , line switch IV, and a variable resistance $R + R'$. Any desired potential can be tapped off by changing the relative resistances in R and R' , and can be applied to the electrolytic cell. A milliammeter, A , is connected in series with the cell to determine the current. In the later work this is replaced by a standard resistance. The potential measurements are made by means of a Leeds and Northrup student type potentiometer. The leads from the potentiometer set-up are connected through the galvanometer, Ga , and key, K , to the middle of the reversing switch, I . The Weston standard cell, V , is the standard for comparison of all measurements. A standard normal calomel electrode, a and b , is placed directly behind each of the two platinum electrodes, $+Pt$ and $-Pt$.

For the benefit of the reader who may wish to trace the circuits represented in Fig. 1, a summary of the manipulation of the switches necessary for the various measurements is given in Table I. To make a given measurement, the switches listed following that measurement should be closed and all others opened. The complexity of the set-up results largely from the fact that it is necessary to break the potentiometer measuring circuit simultaneously with the charge, and also with the discharge, for all measurements.

In order to provide a complete check on the results, it is necessary to measure the fall of potential over every portion of the

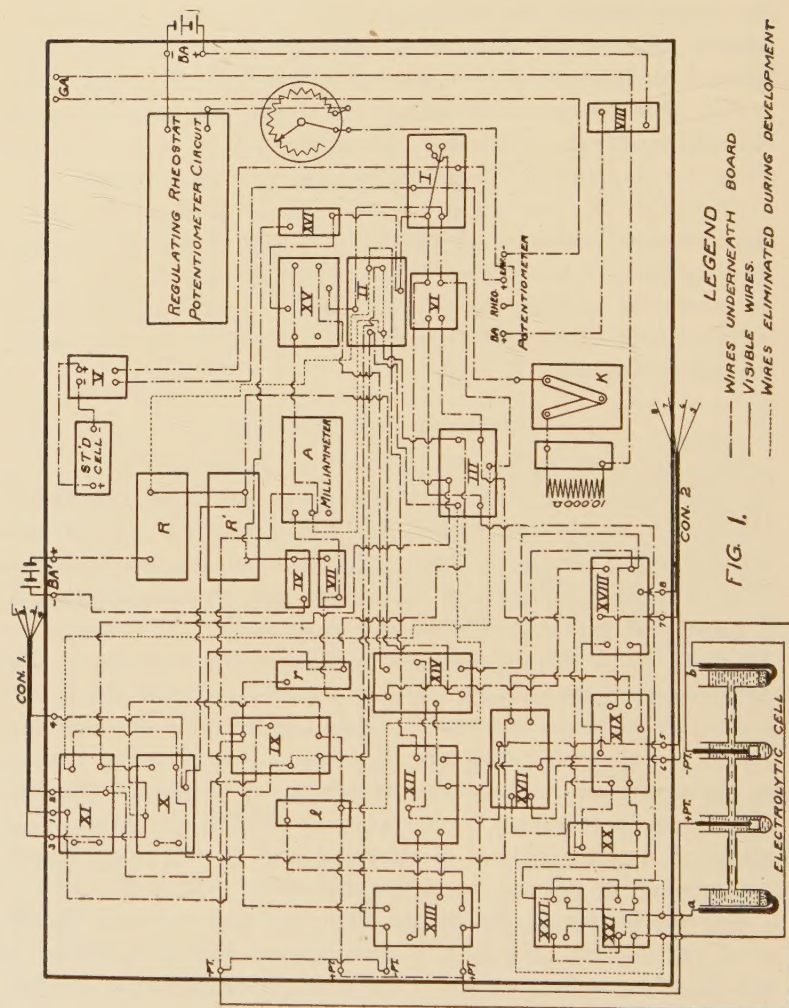


FIG. 1.

charging circuit. The fall of potential over the resistance R' , which is the source of the charging potential, must be found equal to the sum of, (1) the potentials delivered to the two electrodes, (2) the IR drop through the solution, (3) IR drop over brushes, (4) IR drop over ammeter, and (5) the IR drop over all the connecting wires. When this is the case, one may be certain that the apparatus is functioning properly.

TABLE I.

*Switches Which Must Be Closed to Make the Potential Measurements Desired.*A. On charge with the interrupter stationary.
Switches XX and XXII closed.

Potentials to be measured	Switches
Charge.....	I, II (right), XII (right)
+Pt+HgO.....	I, III (left), XII (left), XIII (down)
-Pt-HgO.....	I, III (right), XII (right), XIII (up)
HgO-HgO.....	I, VI
Brushes.....	I, X (right)
Standard Resist....	I, XIV (up), XV (right)
Box R'.....	I, XIV (down), XVI

Switches XX and XXI closed.

+Pt-HgO.....	I, III (left), XII (left), XIII (down)
-Pt+HgO.....	I, III (right), XII (left), XIII (up)

B. On charge with the interrupter rotating.

Charge.....	I, II (right), XII (right), XXII, XX
+Pt+HgO.....	I, III (left), XII (left), XIII (down), XXII, XX
-Pt-HgO.....	I, III (right), XII (right), XIII (up), XXII, XX
HgO-HgO.....	I, VI, XII, XXII
Brushes.....	I, X (right), XVII (left), XXII
Standard Resist....	I, XV (right), XIV (up)
Box R'.....	I, XVI, XIV (down)
+Pt-HgO.....	I, III (left), XII (left), XIII (down), XX, XXI
-Pt+HgO.....	I, III (right), XII (left), XIII (up), XX, XXI

C. On discharge with interrupter rotating.

Discharge.....	I, II (left), IX (down), r
+Pt+HgO.....	I, III (left), IX (down), r, XX, XXII
-Pt-HgO.....	I, III (right), IX (up), XX, XXII
HgO-HgO.....	I, VI, XIII (left), XIX (left), XXII
Standard Resist....	I, XV (left), XVIII (right)
+Pt-HgO.....	I, III (left), IX (down), r, XX, XXI
-Pt+HgO.....	I, III (right), IX (up), r, XX, XXI

An extensive series of measurements was made to test out every part of the set-up. The results were most satisfactory. The sum of the electrode potentials on charge and the fall of potential through the solution equalled the charge potential actually delivered to the cell. The sum of charge potential delivered to the cell, the fall over the brushes, the fall over the standard resistance, and the fall over the lead wires was just equal to the total charge potential or the potential across box R'. The sum of the

electrode potentials on discharge equalled the total discharge potential. The various measurements for the resistance of the solution all gave the same value.

The commutator (Fig. 2) consists of two discs mounted on one shaft. Each disc has two sets of brass and rubber sections; the brass plates on one set are exactly parallel to those on the other.

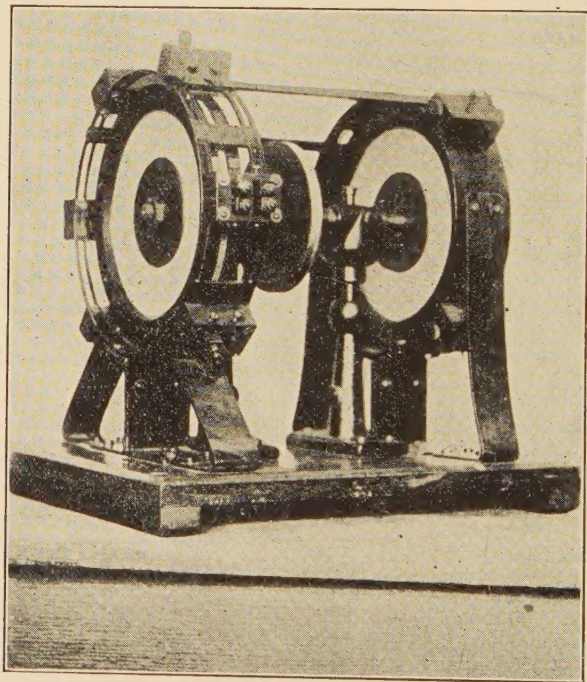


FIG. 2.

With this apparatus it is possible to measure decomposition potentials and overvoltages, by both the direct and commutator methods at the same time and under the same conditions. It was thought, however, that all of the measurements, although they check satisfactorily, might be in error due to the fact that the potentiometer was balanced first against the standard cell directly, and then against the unknown potential when one lead was broken

through the commutator, that is, there might be certain inductive effects introduced by the commutator.

To show that no error was introduced by this arrangement, the standard cell was first balanced in its usual position, and then when put in place of the electrolytic cell (with no current applied, of course). The measured value of the standard cell was found to be exactly the same as that used to obtain the original balance on the potentiometer, whether measured on charge or on discharge, when the interrupter was stationary. When the interrupter was started and the same measurements were made, the measured value was the same as before, both on charge and discharge, no matter what the speed of the interrupter.

All of the measurements up to this time showed that the potential of each electrode on charge was higher than the corresponding value on discharge, and also that the total charge potential was higher than the total discharge potential. This corresponds to what is generally reported in the literature, namely, that the direct method for measuring decomposition potentials gives higher values than the commutator method. Below the decomposition potential the difference is extremely slight, but it increases rapidly above this point.

The principal object of the present investigation is to obtain information which will account for the difference between the values obtained by these two methods. Those who favor the commutator method would probably say that it is due to the existence of a "transfer resistance" between the electrode surfaces and the electrolyte. The subject of "transfer resistance" will be discussed in another paper; it is sufficient to state here that the evidence obtained indicates that there is no such thing as "transfer resistance."

Several experiments were carried out to determine whether the relative sizes of the electrodes has an influence on the difference between the values obtained by the two methods. The solution used was in every case $N/1$ NaOH, and the reference electrodes Hg-HgO- $N/1$ NaOH. For lack of space the data are not included.

In one experiment, the anode, which was large, had a potential about 10 mili. v. higher on charge than on discharge at a current

of 27 mili. amp., while the cathode, which was small, had a potential 203 mili. v. higher on charge than on discharge for the same current (not current density). In another experiment the cathode, which was large, had a potential 11 mili. v. higher on charge than discharge, while the potential for the anode, which was small, was 170 mili. v. higher on charge than discharge at the same current, 30 mili. amp. In yet another experiment in which both electrodes were small and the same size, the cathode was 144 mili. v. higher on charge than on discharge; while the anode gave about the same difference as the cathode (150 mili. v.) between charge and discharge.

The results of this series of experiments show: (1) that the direct method gives higher values than the commutator method; (2) that the differences between the values by these two methods become greater the smaller the electrodes and the higher the applied potential; (3) that the potentials obtained by the commutator method are always higher on charge than on discharge and this difference becomes greater the smaller the electrode and the higher the current.

The important problem to be solved is, what is the cause for the difference between the potentials on charge and discharge? The remaining portion of this paper is an effort to solve this problem. This difference between the charge and discharge potentials might be due to one or more of three factors: (1) the presence of a constant resistance not so far accounted for; (2) the presence of "transfer resistance"; (3) the extremely rapid loss of polarization by the electrodes. The third factor is the only one considered at this time. The first and second factors are discussed in another paper on "transfer resistance."

If the difference is due to the decrease of polarization during the interval between the interruption of the charge potential and the measurement of the discharge potential, then by shortening this time the difference should become less. One method for reducing the time is to use the oscillograph, but this instrument requires too much current for experiments of this nature.

By a slight alteration of the commutator it became possible so to adjust the discharge brushes that the measurements on discharge were taken for only an exceedingly short time either just after the charge brushes left the brass plate or just before the

charge potential was again applied, or during the whole discharge interval. The difference between the first two values gave the loss in potential during a known period of time. It was thus possible to determine the rate of depolarization of the electrodes.

The time during which the value on discharge is measured may be calculated. Since there are three brass segments and three hard rubber segments, all of equal size, the length of time of each discharge interval is $1/r$ p. m./60 $\times$ $1/6$ sec., equals $(10/r$ p. m.) sec. If both discharge brushes are on the brass over only "d" degrees, then the time of each discharge is $(10/r$ p. m.) $\times$ $d/60$ sec. equals $(d/6$ r. p. m.) sec. The discharge value meas-

TABLE II.

Influence of Speed of Rotation of Commutator on Differences Between Electrode Potentials on Charge and Discharge.

Both electrodes small; about 6 mm. $\times$ 1 mm.

Series No.	r. p. m. (1)	I (2)	+Pt (3)	-Pt (4)
1	130	0.00125	0.034	0.0810
2	200	0.00125	0.023	0.0510
3	200	0.00105	0.019	0.0480
4	360	0.00105	0.006	0.0300
5	430	0.00107	0.004	0.0190
6	320	0.00179	0.025	0.0620
7	400	0.00178	0.021	0.0485
8	700	0.00177	0.015	0.0240
9	1350	0.00177	0.005	

ured is the average between the values at the time the discharge circuit is closed, and the time the discharge brushes leave the brass plate. The time interval which corresponds to the average potential measured is $\frac{1}{2}$ of the total interval during which the potential on discharge is measured, or T equals $\frac{1}{2} \times d/6$ r. p. m. equals $(d/12$ r. p. m.) sec. The two discharge brushes, also the two charge brushes, are on the brass at the same time for less than 60 degrees, since the distance between the brushes is about 4 degrees. This means that about 4 degrees are lost at one end of the brass segment.

It is evident from the above formula that T can be altered by varying either r. p. m. or d . If T is decreased by increasing

r. p. m., there should be a corresponding increase in the measured electrode potential, since the time allowed for self depolarization is decreased. This is shown to be the case by the results in Table II.

In Table II, column (1) gives the speed of rotation of the commutator, column (2) the current, column (3) the difference between charge and discharge at the anode, and column (4) the difference between charge and discharge at the cathode. The current and charge potential were constant for series 1 and 2; the same is true for series 3, 4 and 5, only the values are different; also for series 6, 7, 8 and 9.

TABLE III.
Influence of Length of Discharge Interval.

Anode (+Pt)		Discharge Interval in ° d	Cathode (—Pt)		r. p. m.
Charge	Discharge		Charge	Discharge	
.....		40	1.8010	1.790	400
1.122	1.1100	32	1.8010	1.800	400
1.122	1.1170	23	1.8015	1.803	400
1.123	1.1225	14	1.8010	1.809	400
1.123	1.1270	7	1.8020	1.819	400

The results in Table II show that at constant current the difference between the potentials of an electrode on charge and discharge (column 3 and 4) decrease with increase in the speed of rotation of the commutator.

It is possible to change the interval over which the discharge potential is measured by shifting the positions of the brushes. In one position the potential measured is an average discharge potential over a short interval, just after the applied potential is interrupted. This average value increases as r. p. m. is increased. Likewise the average potential of the electrode over a short interval, just before the potential is again applied, is measured by adjusting the brushes to another position. This average value also increases as r. p. m. is increased.

Since the values obtained under the first condition are for the first part of the discharge period, and those obtained under the

second condition are for the last portion of the discharge period, the former should be higher than the latter, and their average should be approximately equal to the values obtained under the condition where the measured value is for the whole period. This last statement is only approximately true, since the rate of self-depolarization is not the same over the whole period. The experiments carried out showed that the statements just made are entirely correct.

The results for one short experiment which is typical of the many performed at this time are included in Table III.

The results in this table show that as the value of d decreases the values for the potentials of the anode (+Pt) and cathode (—Pt) on discharge approach, become equal to and at small values for d exceed their values on charge. The values measured on charge, over 56° of the plate do not change appreciably. As the length of the interval during which the electrodes discharge is shortened, it is to be expected that their potentials should approach and finally become equal to their values on charge; but it is certain that their discharge values can never exceed their true charge values. This indicates that the measured values on charge are too low. The next experiment is an investigation of the potentials on charge.

When the potential of an electrode is measured on charge and the applied potential is suddenly interrupted the potential of the electrode drops several tenths of a volt in one second or less. If the potential is again applied, the electrode does not immediately come to its former value, but several seconds and often even minutes are required. Although the time during which the applied potential is interrupted, when the commutator is in motion, is very short, it seems plausible to assume that the electrode does not come to its full charge value instantaneously when the charge is again applied. It seems probable, therefore, that the measured potential of the electrode is an average between the value it has at the first instant that the potential is applied and the value it has just before the applied potential is interrupted.

The time interval which corresponds to the measured average value is calculated by the formula given above. The average potential applied, during any definite portion of the charge interval, is measured by a proper location of the measuring brushes.

If the brushes in the charging circuit and the brushes which break the potentiometer circuit simultaneously with the charge are in their regular positions, the measured value is the average potential of the electrode on charge over 56° , or practically the whole length of a brass plate. Experiments were carried out in which measurements were made with the charge brushes adjusted to different positions.

The results show that the average values on charge over the last part of the plate are higher than the average values over the whole plate (56°); also, that the average values over the first part of the plate are lower than over the whole plate. The sum of the average value over a certain portion of the first part of the plate, and the average value over an equal portion of the last part, divided by two equals approximately the measured average value over the whole plate. It is evident from these results, that after an electrode has reached such a potential that it loses its charge rapidly, the values measured are in all cases averages. This statement holds true especially for small electrodes or for large electrodes at high current densities.

The values for the electrode potentials over the shortest interval, for the first part of the plate, are the lowest obtained, because the charge potential has just been applied; but as the interval becomes larger the potentials increase, and then, as the shift is made to the last part of the plate the potentials continue to increase as the interval over which they are measured decreases, and reach a maximum at the smallest interval, because here the charge potential has been applied for the longest period; but even here the potential is still less than that obtained by the direct method, that is with the interrupter shorted. *This means that the commutator method can probably never give values for charge potentials which are the same as those obtained by the direct method.* It also means that values for charge potentials obtained by the direct method cannot be used in connection with discharge values obtained by the interrupter method. Just this thing has, however, been done by previous investigators in their calculations of "transfer resistance," and is probably the main cause for the apparent existence of such a "resistance."

The values measured over the last part of the plate on charge, and over the first part of the plate on discharge, become more

nearly equal the smaller the values for d and the more rapid the commutator rotation. In all of these experiments, the values of the electrode potentials measured at the beginning of the discharge interval were greater than the values at the beginning of the charge.

The experiments also show that even the measured current values are averages. When a cell with a low definite potential is interrupted for even a short time, the potentials of the electrodes decrease. If the potential is again applied, the current is higher at first, and then decreases as the potentials of the electrodes increase. The same thing happens when the interrupter is rotating, though of course the time interval during which the applied potential is interrupted is very short.

In order to confirm the various statements which have been made, several series of experiments were carried out, in which practically every type of measurement made in the previous work is included. The measurements in each set of experiments were made under the same conditions and are therefore comparable. For lack of space, only about the last third of the results of only one such experiment is included in this paper (Table IV). In this experiment two small electrodes were used.

In every series of readings thirty-seven potential measurements were made in rapid succession after the applied potential had become constant. The measurements in section 1 of the table include the potentials on charge with the interrupter shorted; section 2, those on charge and discharge over 56° of the plates; section 3, those over the last 15° , and section 4, those over the first 15° . The measurements were made in this order. The order of measurements in each section is indicated by the column numbers.

The results in these tables confirm in every respect conclusions drawn from previous tables. In each section the sum of the electrode potentials (columns 2 and 3) on charge, and the IR drop through the solution (column 6), equals the applied potential (column 1), and the sum of the potentials of the electrodes on discharge (columns 9 and 10) equals the discharge potential (column 8). The values for the IR drop through the solution, obtained by subtracting the electrode potentials (2 and 3) from the corresponding values obtained by measuring the potential of

TABLE IV.—*Summary Table. Small Electrodes.*

SECTION 1—Interrupter Stationary. Potentials Are Those Obtained by the Direct Method.

Series No.	Time	Ratio R:R	Time	Charge (1)	+Pt +HgO (2)	-Pt -HgO (3)	+Pt -HgO (4)	-Pt +HgO (5)	HgO -HgO (6)	I (7)	Cell R (11)
	12/19/22										
1	*11:25	750-900	11:50	2.2350	1.0558	1.0988	1.1362	1.1790	0.0800	0.0010052	79.59
2	*12:15	900-900	2:20	2.3100	1.0776	1.1322	1.1780	1.2326	0.1002	0.001340	74.78
3	*2:55	1000-600	3:35	2.5030	1.1120	1.1886	1.3136	1.3901	0.2012	0.002749	73.19
4	*5:15	1000-400	6:05	2.7095	1.1483	1.2522	1.4578	1.5615	0.3095	0.004245	72.92
6	*9:45	1000-200	10:38	3.1380	1.2245	1.3670	1.7724	1.9150	0.5475	0.007230	75.72
	12/20/22										
7	*11:15	1000-100	9:40 A.M.	3.7246	1.3192	1.6990	2.0250	2.4056	0.7055	0.009389	75.14

SECTION 2—Interrupter Rotating, Potentials Measured Over Whole Plate by Commutator Method

Series No.	Time	Charge (1)	+Pt +HgO (2)	-Pt -HgO (3)	+Pt -HgO (4)	-Pt +HgO (5)	HgO -HgO (6)	I (7)	Discharge (8)	+Pt +HgO (9)	-Pt -HgO (10)	Cell R (11)
1	11:55	2.1942	1.0361	1.0724	1.1217	1.1581	0.0861	0.001130	2.0865	1.0245	1.0614	76.20
2	2:30	2.2610	1.0550	1.0987	1.1614	1.2055	0.1065	0.001425	2.1242	1.0400	1.0847	74.74
3	3:45	2.4524	1.0910	1.1518	1.2995	1.3597	0.2085	0.002852	2.1776	1.0572	1.1205	73.11
4	6:08	2.6450	1.1260	1.2010	1.4452	1.5290	0.3190	0.004377	2.2300	1.0732	1.1562	72.86
5	9:15	2.7000	1.1434	1.2415	1.4565	1.5545	0.3130	0.004265	2.2735	1.0890	1.1842	73.39
6	10:45	3.1000	1.2025	1.3363	1.7630	1.8965	0.5605	0.007357	2.3548	1.1180	1.2347	76.19
	12/20/22											
7	9:50	3.6700	1.2835	1.6635	2.0054	2.3850	0.7220	0.009612	2.6460	1.1655	1.4795	75.11
8	11:05	3.6690	1.2795	1.6766			0.7120	0.009623	2.6670	1.1655	1.4990	74.00

SECTION 3—Interrupter Rotating, Measurement Made Over the Last 15° ± 1, Commutator Method

Series No.	Time	Charge (1)	$\frac{+Pt}{+HgO}$ (2)	$\frac{-Pt}{-HgO}$ (3)	$\frac{+Pt}{+HgO}$ (4)	$\frac{-Pt}{-HgO}$ (5)	$\frac{HgO}{-HgO}$ (6)	I (7)	Discharge (8)	$\frac{+Pt}{+HgO}$ (9)	$\frac{-Pt}{-HgO}$ (10)	Cell R (11)
	12/19/22											
1	12:01	2.2101	1.0466	1.0807	1.1297	1.1637	0.0837	0.001097	2.0687	1.0135	1.0548	76.30
2	2:37	2.2812	1.0673	1.1095	1.1708	1.2132	0.1040	0.001390	2.1010	1.0267	1.0740	74.81
3	3:53	2.4800	1.1058	1.1696	1.3095	1.3735	0.2040	0.002791	2.1435	1.0402	1.1030	73.09
4	6:15	2.6880	1.1425	1.2350	1.4550	1.5475	0.3130	0.004284	2.1840	1.0535	1.1306	73.06
5	9:20	2.7364	1.1593	1.2702	1.4652	1.5760	0.3064	0.004166	2.2242	1.0680	1.1560	73.55
6	10:55	3.1380	1.2210	1.3655	1.7730	1.9180	0.5540	0.007201	2.2940	1.0930	1.2002	76.93
	12/20/22											
7	10:05	3.7016	1.2980	1.6930	2.0070	2.4016	0.7082	0.009452	2.5602	1.1335	1.4270	74.93
8	11:15	3.7000	1.2950	1.7055			0.6970	0.009450	2.5760	1.1335	1.4415	73.76

SECTION 4—Interrupter Rotating, Potentials Measured Over the First 15°, Commutator Method

Series No.	Time	Charge (1)	$\frac{+Pt}{+HgO}$ (2)	$\frac{-Pt}{-HgO}$ (3)	$\frac{+Pt}{+HgO}$ (4)	$\frac{-Pt}{-HgO}$ (5)	$\frac{HgO}{-HgO}$ (6)	I (7)	Discharge (8)	$\frac{+Pt}{+HgO}$ (9)	$\frac{-Pt}{-HgO}$ (10)	Cell R (11)
1	12:07	2.1730	1.0212	1.0630	1.1098	1.1522	0.0886	0.001172	2.1096	1.0375	1.0720	75.60
2	2:45	2.2310	1.0366	1.0843	1.1467	1.1940	0.1100	0.001481	2.1529	1.0550	1.0970	74.27
3	4:00	2.4026	1.0625	1.1240	1.2775	1.3395	0.2145	0.002952	2.2265	1.0808	1.1456	72.66
4	6:23	2.5870	1.0890	1.1660	1.4210	1.4970	0.3032	0.004555	2.2905	1.1005	1.1895	66.56
5	9:30	2.6244	1.1040	1.1930	1.4305	1.5205	0.3268	0.004455	2.3410	1.1175	1.2224	73.35
6	11:05	3.0240	1.1610	1.2750	1.7495	1.8640	0.5888	0.007626	2.4430	1.1565	1.2860	77.21
7	10:15	3.5570	1.2280	1.5665	1.9900	2.3272	0.7620	0.010202	2.7700	1.2080	1.5595	74.70
8	11:20	3.5570	1.2255	1.5810			0.7510	0.010190	2.7770	1.2060	1.5740	73.70

each electrode against the opposite standard, and thus including the IR drop through the solution (columns 4 and 5), agree well with the values of the IR drop obtained by measuring the potential between the two standard electrodes (column 6).

Before one of these experiments (the data for which are not recorded in this paper) was performed, the resistance of the cell was determined by the Kohlrausch method, and was found to be 78.2 ohms. After the experiment the resistance was again determined, and found to be 80.1 ohms. The resistance calculated from any of the values for the IR drop through the solution was the same, within the limits of experimental error as the value by the Kohlrausch method.

The tables also show that in each series all of the values measured over 56° (section 2) of the plate, are approximately the averages of those in sections 3 and 4. Even the resistance of the cell as calculated in 2, 3 and 4 makes it appear that the values in 2 are the averages of those in 3 and 4.

CONCLUSIONS.

The conclusions to be drawn from this work are: (1) The absolute values obtained by the commutator method are practically meaningless, since they depend upon the mechanical construction and operation of the commutator. (2) There is a decided indication that the commutator and direct methods would give the same measured values if the measurements by the commutator method could be made at the instant the charging circuit is interrupted. Further work is now in progress along this line.

¹ paper presented at the Forty-seventh General Meeting of the American Electrochemical Society, held at Niagara Falls, April 25, 1925, President H. C. Parmelee in the Chair.

TRANSFER RESISTANCE.¹

By A. L. FERGUSON and GERRIT VAN ZYL.²

ABSTRACT.

The idea of "transfer resistance" was first introduced into the literature by Gore in 1885. Since then it has been given some attention by several investigators. The idea has been much studied and its significance pointed out by many during the last few years. Newbery is the leading supporter. Transfer resistance developed from the observations that the discharge potentials measured by the commutator method are always less than the charge potentials. It is shown by the data in the present paper that the differences between the charge and discharge values is not due to a constant resistance. It is further shown that the charge and discharge values are the same, and therefore that there is no such thing as "transfer resistance."

In an earlier article³ the authors described an apparatus which makes possible the measurement of decomposition potentials by both the direct and commutator methods at the same time. It is also possible to determine how the total potential is distributed between the anode and cathode. By means of this apparatus data have been obtained which throw light upon the question of "transfer resistance."

The concept of "transfer resistance" was introduced by Gore,⁴

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³ Trans. Am. Electrochem. Soc., **45**, 311 (1924).

⁴ Proc. Roy. Soc., **38**, 209 (1885).

and has been discussed by many others since that time.⁵ During the last few years the subject of "transfer resistance" has been extensively studied by Edgar Newbery,⁶ of England. In a reply to two articles by MacInnes⁷ on the subject of overvoltage, he states "*Overvoltage* is of necessity an *active* voltage or e. m. f., capable of doing work after all external sources of e. m. f. have been removed. Transfer resistance is a purely *passive* or frictional force, which entirely ceases when the external e. m. f. is interrupted. These two forces work in the same direction during the passage of the current; but directly the current is interrupted, overvoltage alone exists and may be measured. Although overvoltage and transfer resistance occur together in this way, they are mutually independent and frequently vary in opposite directions."

Later in the discussion he states, "Since the surface area of the electrodes used was very small (no definite data are given) the transfer resistance at the electrode must have amounted to at least 1,000 ohms, and may have been 100,000 ohms. Under these conditions, therefore, the effect of overvoltage is negligible, and the whole work of the authors has consisted in measuring, not overvoltage, but the excess potential required to overcome transfer resistance." In the course of his reply to the criticism of Newbery, MacInnes states, "It is evident that the concept of 'transfer resistance' should receive careful consideration." Later in the reply he states " . . . Newbery himself points out quite logically . . . that the existence of 'transfer resistance' at the surface of electrodes means that all conductance measurements are in error. . . . These transitory resistances are of surprising magnitude, being as high as 1,000 ohms for cells containing solutions whose resistances are of the order of 10 ohms." These quotations are given because they express so well the meaning and the significance of this concept "transfer resistance."

⁵ Burgess, *Trans. Am. Electrochem. Soc.*, **7**, 51 (1905); Franklin and Freudenberger, *Trans. Am. Electrochem. Soc.*, **7**, 33 (1905); Addicks and Freudenberger, *Trans. Am. Electrochem. Soc.*, **8**, 227 (1905); Coffetti and Foerster, *Ber. deutsch. chem. Ges.*, **38**, 2934 (1905); Sand and Black, *Z. physikal. Chem.*, **70**, 496 (1910); Pring, *Z. Elektrochem.*, **19**, 225 (1913); Chany, *Trans. Am. Electrochem. Soc.*, **29**, 181 (1916); Foerster, *Z. Elektrochem.*, **17**, 881 (1911); Newbery, *Trans. Faraday Soc.*, **15**, 126 (1919); Newbery, *J. Am. Chem. Soc.*, **42**, 2007 (1920); Newbery, *J. Chem. Soc.*, **121**, 7 (1922); Tartar and Keyes, *J. Am. Chem. Soc.*, **44**, 557 (1922); Glasstone, *J. Chem. Soc.*, **123**, 1745, 2926 (1923); **125**, 250 (1924).

⁶ *J. Am. Chem. Soc.*, **42**, 2007 (1920).

⁷ *J. Am. Chem. Soc.*, **41**, 194, 2013 (1919).

According to Newbery, the total resistance of an electrolytic cell is made up of two parts, the ordinary electrolytic resistance and "transfer resistance." He calculated the total resistance by dividing the difference between the applied potential and the counter or polarization potential (which difference he evidently considered as due entirely to an IR drop) by the current. The ordinary electrolytic resistance was obtained from conductivity data. The difference between this electrolytic resistance and the total resistance is what he called "transfer resistance."

A careful examination of Newbery's method for obtaining the data necessary to make the calculations is advisable. As stated above, the total potential applied to the cell and the total potential which the cell delivers when the applied potential is interrupted must be known. The values for the latter, which he called counter e. m. f., were calculated by adding to the theoretical decomposition potential the sum of the anodic and cathodic overvoltages. These overvoltages were in some cases measured and in others obtained from tables. The applied potential was measured without a commutator in the circuit, at a current density corresponding, as nearly as could be determined, to that used when the overvoltages were determined. It is extremely doubtful, however, whether the counter e. m. f. calculated in this way represents a true value which may be used with the measured applied potential to calculate "transfer resistance." From our own work it appears also extremely doubtful whether even the applied potential is the same with and without a commutator in the circuit.

All measurements on decomposition potentials and overvoltages show that polarization values change at first very rapidly with time, and later more slowly. Measurements of these quantities should be made, therefore, after sufficient time has been allowed for these changes to have taken place. The time factor, which is undoubtedly the most disturbing and confusing of all of the factors which influence overvoltage and polarization values, would thus be largely eliminated. This plan was followed in the work described in this article. A large number of experiments were carried out in which various factors were changed, such, for instance, as nature and concentration of electrolyte, relative sizes of electrodes, speed of commutator, etc.

Table I shows the type of measurements made and results obtained. The table is divided into three sections. Section A contains measurements made with the commutator stationary, or, in other words, they are values obtained by the direct method. The measurements in Sections B and C are made with the commutator rotating, or they represent the values by the commutator method.

TABLE I.

Decomposition Potentials by the Direct and Commutator Methods.

SECTION A.

Measurements in columns up to and including (10) made on charge with interrupter stationary (direct method). Cathode 2.5 x 0.5 cm. Anode 2.5 x 0.5 cm. Electrolyte, normal NaOH.

Time	Ratio R — R'	Total Charge	Anode Pot. + Pt + HgO	Cathode Pot. — Pt — HgO	Sum (2) + (3)	Anode Pot. + IR drop through solution + Pt — HgO (5)
		(1)	(2)	(3)	(4)	(5)
3/29/22 *10.15 P. M...	1000-800					
3/30/22 9.00 A. M...		1.9957	0.8235	0.960	1.7835	1.033
8.00 P. M...		2.2025	0.860	0.9623	1.8223	1.2396
*8.30.....	1000-400					
3/31/22 12.00.....		2.454	0.8991	0.9684	1.8675	1.4865
*12.30.....	1000-200					
5.30.....		3.320	0.952	0.9822	1.934	2.340

SECTION A—Continued

Difference (5) — (2)	Cathode Pot. + IR drop through solution — Pt + HgO	Difference (6) — (3)	IR drop over charge brushes Ch. Br.	IR drop over standard resistance A. Box	IR drop through solution + HgO — HgO	IR drop over charging resistance (R') B Per Ct.
(5)'	(6)	(6)'	(7)	(8)	(9)	(10)
0.210	1.170	0.210		0.030	0.212	2.027
0.379	1.3422	0.380	0.0108	0.0531	0.3777	2.266
0.587	1.5555	0.587	0.0296	0.0895	0.5872	2.579
1.388	2.368	1.386	0.0368	0.2064	1.3866	3.607

SECTION B.

Measurements in columns (11) to (20) made on charge with interrupter rotating.

Total Charge (11)	+ Pt + HgO (12)	— Pt — HgO (13)	Sum (12 + 13) (14)	+ Pt — HgO (15)	Difference (15) — (12) (15)'	— Pt + HgO (16)
1.959	0.7932	0.9542	1.7474	1.005	0.202	1.1655
2.167	0.8315	0.9555	1.7870	1.212	0.381	1.337
2.423	0.870	0.9604	1.8304	1.464	0.594	1.5535
3.302	0.927	0.9726	1.8996	2.338	1.411	2.294

SECTION B—Continued

Difference (16) — (13) (16)'	Ch. Br. (17)	A. Box (18)	+ HgO — HgO (19)	B. Pot. (20)
0.211	0.024	0.0301	0.2108	2.015
0.382	0.026	0.0536	0.3805	2.253
0.593		0.0907	0.592	2.562
1.321		0.202	1.400	3.600

SECTION C.

Measurements in columns (21) to (26) made on discharge with interrupter rotating.

Total Discharge (21)	+ Pt + HgO (22)	— Pt — HgO (23)	Sum (22 + (23) (24)	+ Pt — HgO (25)	— Pt + HgO (26)
1.7463	0.7928	0.9539	1.7467	0.7928	0.9538
1.7840	0.8295	0.9547	1.7842	0.8293	0.9548
1.8255	0.8675	0.9577	1.8252	0.8680	0.9585
1.8890	0.9206	0.9668	1.8874	0.9212	0.9680

In the column headed Time, the figures marked with an asterisk show the times at which the applied potential was increased; the other figures indicate the times of making the measurements. It should be noted that several hours elapsed between these times. Other workers have allowed only a few seconds or a few minutes at most.

The numbers in the column headed Ratio indicate the resistances in the two series boxes R and R' respectively.⁸ These resistances serve as a potentiometer effect to change the applied or charge potential. In column (1) are the charge potentials actually delivered to the cell; column (2) shows the portions delivered to the anode, and column (3) the portions delivered to the cathode. Column (4) contains the sums of the values in (3) and (2), and should equal the charge potential (column 1) minus the IR drop through the solution (column 9). An inspection of the values shows an extremely good agreement.

The values in column (5) are obtained by measuring the potential between the *anode* and the reference electrode back of the *cathode*; these values, therefore, contain the electrode potential and the IR drop through the solution. Column (6) contains values for the cathode similar to those in (5) for the anode. The differences (column (5)') between the values in columns (5) and (2), and the differences (column (6)') between (6) and (3) should give the IR drop through the solution and should equal the corresponding values in (9). The agreement here is most satisfactory. For the commutator rotating, the IR values are in columns (15)', (16' and (19). A comparison between these and corresponding values in columns (5)', (6)' and (9) for the commutator stationary shows they agree very well. This shows that the commutator causes no change in the IR drop between the electrodes.

Column (7) contains values for IR drop over the charge brushes on the commutator. In column (8) are the values for the IR drop over the standard resistance (10.45 ohms) from which the current may be calculated. Column (10) contains the values for the IR drop over the resistance R', which is the source of the charging potential. The values in this column should equal the sums of the corresponding values in columns (4), (7), (8) and (9). The agreement is good in this table, but in later work in which the IR drop over the connecting wires is considered it is practically complete. The columns in Sections B and C are so similar to corresponding columns in Section A that a separate description is not necessary. The values agree among themselves equally well for the commutator rotating, that is in Sections B and

⁸ Trans. Am. Electrochem. Soc., 45, 313 (1924).

C, as for the commutator stationary. The close agreement between corresponding values in columns (22) and (25), also between (23) and (26) show there is nothing of the nature of an IR drop through the solution on discharge, which, of course, is to be expected, but which may not always be the case.

When the commutator method is used, it is to be expected that the measured total discharge potential (column 21) should equal the sum of the electrode potentials on discharge (column 24), and also the sum of the electrode potentials on charge (column 14). The table shows that the first of these, that is, the sum of the electrode potentials on discharge, does equal the measured total discharge potential, but that the second does not hold, that is, these values are in all cases less than the sum of the electrode potentials on charge. This difference is small, yet real, at low current densities, and increases materially with increase in current density. Another significant point to be observed is that both the discharge and charge potentials, columns (24) and (14), measured by the commutator method are less than the corresponding potentials measured by the direct method, column (4), and this difference increases with increase in applied potential. These differences are explained by many on the basis of "transfer resistance." A consideration of these differences is the primary object of this paper.

Some have suggested that the operation of the commutator itself might introduce errors due to induction, capacity or static effects. A few experiments were made to test this. The potentiometer was first balanced against an old standard cell, then this same cell was introduced in place of the decomposition cell, and its value determined with the interrupter shorted, or this amounts to the ordinary potentiometer set-up. The value found, of course, was the same as that assumed in balancing the potentiometer. The value was then measured through the charge brushes and also through the discharge brushes for various speeds of the interrupter. Other experiments were tried in which two standard cells were used in series, and in which one and two dry cells were used, each at various speeds of the interrupter. In these cases the values obtained under the different conditions showed a maximum variation of less than two millivolts, and in most cases the variation was

only a few tenths of a millivolt. It is evident that the interrupter introduces no new sources of potential greater than other experimental errors.

TABLE II.

Measurement of Apparent Constant Resistance.

Commutator speed, 600 r.p.m. Both electrodes same size, large, about 0.5 by 2.5 cm.

Anode charge minus discharge $\Delta + \text{Pt}$ (1)	Current I (2)	$\frac{\Delta + \text{Pt}}{I}$ (3)	Cathode charge minus discharge $\Delta - \text{Pt}$ (4)	$\frac{\Delta - \text{Pt}}{I}$ (5)
0.007	0.0112	0.625	0.0034	0.303
0.0235	0.0298	0.788	0.015	0.503
0.041	0.0509	0.805	0.026	0.510
0.0545	0.0635	0.858	0.033	0.519
0.0635	0.0695	0.912	0.038	0.546

TABLE III.

Measurement of Apparent Constant Resistance.

Commutator speed 600 r.p.m. Both electrodes small, 6.5 by 1 mm.

Anode charge minus discharge $\Delta + \text{Pt}$ (1)	I (2)	$\frac{\Delta + \text{Pt}}{I}$ (3)	Cathode charge minus discharge $\Delta - \text{Pt}$ (4)	$\frac{\Delta - \text{Pt}}{I}$ (5)
0.005	0.00124	4.030	0.0035	2.823
0.049	0.0102	4.804	0.038	3.725
0.092	0.0188	4.851	0.084	4.468
0.191	0.0402	4.751	0.224	5.572
0.255	0.0545	4.862	0.285	5.229

The difference between the potentials of the electrodes on charge and discharge might be due to the presence of a constant resistance, the IR drop over which is included in the measured charge potential, but not in the discharge potentials. This would result in a smaller potential actually available to charge the electrodes than the one measured. Many experiments were performed in which the IR drops over every part of the charging circuit were measured, even including lead wires, and it was found that their sum, when added to the measured electrode potential values on charge, which were actually effective in charging the

electrodes, was exactly equal to the source of charging potential, namely, the IR drop over R' . The only remaining possible source then of such a disturbing resistance is between the rear metal surface of the electrode and the standard reference electrode. If such a resistance exists it should be possible to calculate it by dividing the difference between the charge and discharge values by the current. Several experiments of this nature were carried out. A few of the results of two of these are included in Tables II and III.

The only difference between the two experiments, the results of which are recorded in these tables, is in the size of the electrodes. Column (1) in each table contains the differences between charge and discharge potentials at the anode; column (2) the current; column (3) the calculated apparent resistance at anode; columns (4) and (5) correspond to (1) and (3) for the cathode. The results show that the apparent resistance is fairly constant, for electrodes of the same size, over a wide range of current and potential differences. The value of the resistance is smaller the larger the electrodes. From these experiments one might be inclined to conclude that there is a constant resistance between the reference electrode and the rear face of the polarized electrode; but in reality all they show is that the difference between the charge and discharge potential at each electrode is approximately proportional to the current.

If this difference is really due to an IR drop over a constant resistance, then it should not change with the speed of the commutator at constant current. Several experiments were carried out to test this. A sample of the results is shown in Table IV. In series (2) the current is held the same (0.00125 amp.) as in series (1) while the speed of the commutator is increased. The calculated resistances (columns 4 and 6) decrease with this increase in speed of the commutator. The current is the same in series (4) as in series (3), also the same in series (6) as in (5), but in each of these cases, as in series (1) and (2) the calculated resistance decreases with increase in the speed of the commutator.

It appears from these experiments that the difference between the electrode potentials on charge and discharge is not due to a *constant* resistance. The results so far, however, do indicate that the difference may be due to a resistance which changes with con-

ditions. This is a characteristic of the so-called "transfer resistance."

If the difference between the electrode potential on charge and discharge can be explained by "transfer resistance" and if "transfer resistance" ceases when the external circuit is interrupted, as Newbery claims it does, then a change of speed of commutator rotation at constant current should have no effect upon it. From the results in Table IV, however, it is evident that even for the same current the differences between the potentials of the electrodes on charge and discharge decrease as the speed of the commutator increases. This argues against the differences being due to "transfer resistance."

TABLE IV.

Influence of Speed of Rotation of Commutator on the Apparent Resistance.

Electrolyte, normal NaOH. Both electrodes small, about 6 mm. by 1 mm.

Series No.	R. P. M. (1)	$\Delta + \text{Pt}$ (2)	I (3)	$\frac{\Delta + \text{Pt}}{I}$ (4)	$\Delta - \text{Pt}$ (5)	$\frac{\Delta - \text{Pt}}{I}$ (6)
1	130	0.034	0.00125	27.2	0.081	64.8
2	200	0.023	0.00125	18.4	0.051	40.8
3	200	0.019	0.00105	18.0	0.048	45.7
4	430	0.004	0.00107	3.7	0.019	17.8
5	320	0.025	0.00179	13.96	0.062	34.64
6	700	0.015	0.00177	8.5	0.024	13.56

In one of Newbery's publications⁹ several tables are given containing calculated values for "transfer resistance." In one experiment the conditions were practically the same as in one of ours. Using the same method of calculation, we obtained a "transfer resistance" of 4.56 ohms per sq. cm. at a current density of 33 milliamperes where he gives 9, and at 5 milliamperes we obtained 3.3 ohms where he gives 70 ohms. For 2 milliamperes he gives 120 ohms, while our values remained practically unchanged. This marked disagreement is most likely the result of two factors: (1) difficulties inherent in the apparatus used by Newbery, which made it impossible to obtain the true potentials, and (2) sufficient time

⁹ Trans. Farad. Soc., **15**, 126 (1919).

was not allowed by Newbery for the electrodes to come to equilibrium.

This whole concept of "transfer resistance" has probably developed as a result of two sources of error, which were not evident at the time calculations were made by the different investigators. The most general error is the use of potential values measured at different times and under different conditions, and therefore not comparable. For instance, the counter e. m. f. of a cell or electrode was usually calculated by adding the over-voltage, obtained from published tables, to the theoretical decomposition potential. This sum, or counter e. m. f., was then subtracted from the applied e. m. f., measured at a different time and under different conditions, to secure a value from which "transfer resistance" was calculated. The present work has definitely shown that the conditions which would be different, such as time of polarization, nature of electrode surface, size of electrodes, etc., have a most important influence on these values. Hence potentials determined in the above manner are not comparable. The second source of error, it will be shown later, is inherent in the apparatus used for measuring counter e. m. f. directly.

In the work described in this paper all of the potentials required in the calculation were measured simultaneously and strictly under the same conditions. The first source of error was thus eliminated, but there still remained a difference between the charge and discharge values at each electrode. The difference would be interpreted by some as due to "transfer resistance." The remainder of this paper is an attempt to show that it is due to an inherent source of error in the apparatus used for measuring the counter e. m. f. directly.

It is assumed in the commutator method that the potential measured when the charging current is flowing is the potential effective in charging the electrodes, also that the potential measured on discharge with the commutator is the actual discharge potential. If the charge potential is not constant, but increases during the charge period, or if the electrodes discharge during the interval of interruption of the charging potential, then these assumptions are not justified. The following experiments and discussion show that this is the case.

TABLE V.

*Variation of Charge and Discharge Potentials with Time
and with R. P. M.*

SECTION A.

Charge and discharge intervals whole length of plates.

R. P. M.	Series	Anode charge 1	Anode discharge 2	Diff. (1) — (2) 3	Cathode charge 4	Cathode discharge 5	Diff. (4) — (5) 6
800	I	1.115	1.091	0.024	1.551	1.536	0.015
800	II	1.117	1.092	0.025	1.550	1.535	0.015
400	III	1.118	1.082	0.038	1.553	1.533	0.020
400	IV	1.120	1.083	0.037	1.553	1.533	0.020

SECTION B.

Charge and discharge intervals the last 14° of plates.

R. P. M.	Series	Anode charge 7	Anode discharge 8	Diff. (7) — (8) 9	Cathode charge 10	Cathode discharge 11	Diff. (10) — (11) 12
800	I	1.148	1.061	0.087	1.565	1.520	0.045
800	II	1.150	1.062	0.088	1.564	1.519	0.045
400	III	1.160	1.041	0.119	1.573	1.512	0.061
400	IV	1.162	1.039	0.123	1.573	1.511	0.062

SECTION C.

Charge and discharge intervals the first 14° of plates.

R. P. M.	Series	Anode charge 13	Anode discharge 14	Diff. (13) — (14) 15	Cathode charge 16	Cathode discharge 17	Diff. (16) — (17) 18
800	I	1.080	1.123	—0.043	1.531	1.549	—0.018
800	II	1.084	1.126	—0.042	1.532	1.550	—0.018
400	III	1.064	1.128	—0.064	1.526	1.554	—0.028
400	IV	1.065	1.128	—0.063	1.525	1.554	—0.029

SECTION D.

Charge on continuously (direct method).

	Series	Anode charge 19	Diff. (19) — (7) 20	Cathode charge 21	Diff. (21) — (10) 22	
	I	1.229	0.081	1.600	0.035	
	II					
	III	1.225	0.065	1.601	0.028	
	IV					

The commutator was so built that the various brushes could be adjusted to any position relative to one another. By this arrangement the total charge potential or the charge at either anode or cathode could be measured during the whole charge interval or during any measured portion of it. It could thus be determined whether the charge remained constant or varied during the charge interval. Precisely the same arrangement was likewise made for the discharge potentials.

These various intervals could also be changed, and by measurable amounts, by adjusting the speed of the commutator. The length of any interval in seconds is given, for our particular commutator, by the formula, time in seconds = $d/12$ r. p. m., where d is the number of degrees during which both brushes are on a brass segment and r. p. m. has its usual meaning.

A large number of experiments were carried out involving, (1) different concentrations of acids, bases, and salts; (2) wide ranges of commutator speed; (3) numerous variations in length and position of charge and discharge intervals over which the potentials were measured; (4) a wide range of current density; (5) variations in size and nature of surface of electrodes. To economize space, the results of only one of these experiments will be given here. These are contained in Table V.

This table purposely contains only a small amount of data, but it may be considered, in a way, as a summary table because the data here recorded are typical of a large mass of similar data. Any observations or conclusions made from this table should be considered as substantiated by all of the unrecorded results. There is no exception to this statement.

The only data recorded are the anode and cathode potentials measured under eight different sets of conditions, since these are the ones most pertinent in this discussion. Two different sets of conditions are involved in each of the four sections (A, B, C, D); one pertains to the portion of charge and discharge interval over which measurements were made, and the other to r. p. m. of commutator. In Sections A, B, C, the ones in which the commutator was used, the measurements in series I and II were made with a commutator speed of 800 r. p. m.; in series III and IV, with a speed of 400 r. p. m. In Section A all potentials were measured

during the *whole* of the charge or discharge interval, that is, during the time required for all the brass segments of the commutator to pass under the brushes. Section B contains similar data, except that the measurements were made only over the *last* 14° of the commutator plates. In Section C the measurements were made over the *first* 14° . In D the commutator was short-circuited, that is, the charging current was on all the time. The measurements in Sections A, B and C represent values obtained by the commutator method, while those in the last section represent values obtained by the direct method.

The data in this table bring out many interesting points. All of the separate generalizations, however, support the one fundamental conclusion that the differences between the various potentials measured by the commutator and direct methods are due to sources of error inherent in the commutator method. As these sources of error are reduced in magnitude the differences become less and would ultimately disappear, and, from the very nature of the case, "transfer resistance" would vanish at the same time. Some of the individual generalizations will now be pointed out.

First consider the data in series I, that is, with a constant speed of 800 r. p. m. When the time interval extends over nearly the whole of the segment, or about 56° , the value of the anode charge (column 1) is 1.115 v.; when the measurement is made over the last 14° of the segment (column 7), the value is 1.148 v., or 0.033 v. *higher* than over the whole segment; and when measured over the first 14° (column 13) the value is 1.080, or 0.035 v. *lower* than over the whole segment. In other words, the potential which is actually effective in charging the anode increases 0.068 v. during the time it takes the segment to move through 46° , *i. e.*, from the middle of the first 14° , or 7° from the beginning of the segment to the middle of the last 14° , or 7° from the end of segment, or less than 0.01 second. The increase at the cathode during this same time, calculated from columns 10 and 16, is 0.034 v. The inevitable conclusion is that all charge potentials measured by the commutator method are average values and can never equal the potential actually effective in charging the electrode.

An analysis of corresponding data for the cathode (columns 4, 10 and 16) shows that precisely the same conclusion applies to this

electrode. The *discharge* potentials measured during these same three portions of the discharge interval are given in columns 2, 8 and 14 for the anode and 5, 11 and 17 for the cathode. An analysis of the data in these columns shows that the anode discharge potential decreases during this same time interval (46°) by 0.062 v. and the cathode by 0.029 v. It is evident that the discharge values given by the commutator method must also be averages and that this method can not give the true discharge values of an electrode.

The data in series III, obtained with a slower speed (400 r. p. m.) lead to the same conclusions as series I just discussed, except that the effects are more pronounced, due to the slower rate of rotation, and thus a longer time for the increase in charge and decrease in discharge to take place.

After the measurements in series I were made they were immediately repeated and the values appear in series II. A similar statement applies to series III and IV. It may be observed that the values in II are slightly different from those in I; and a corresponding difference exists between series IV and III. This is due to the fact that the values all change slightly with time.

The data in section D are obtained by the direct method or with the charging current on all the time. It is to be expected that these values would be larger than those obtained with the commutator. In fact it is our belief that these are the limits towards which the charge values approach, and from which the discharge values start. The data are not complete enough (due to inherent limitations of the apparatus) to prove this conclusively. It may be observed, though, that the difference (column 20) between the highest anode charge value obtained with the commutator (column 7) and the value by the direct method (column 19), is only 0.065, while the charge increased, as pointed out above, 0.068 v. during the time it took the segment to travel 46° . The difference between the highest discharge value (column 14) and the value by the direct method (column 19) is 0.097, and the discharge dropped 0.087 v. during the time it took the segment to move 46° .

It is interesting to note that the highest measured discharge values for anode, 1.128 v. (column 14), and for cathode 1.554 v. (column 17), are actually higher than the corresponding lowest

charge values (columns 13 and 16) by 0.063 v. and 0.029 v. respectively. "Transfer resistance" on the basis of these figures would be negative.

The data in this table demonstrate almost conclusively that the discharge potential of an electrode would be the same as the charge potential if the two could be measured at the same instant by the commutator method, and that both would be the same as the value by the direct method. This leads inevitably to the conclusion that there is no such thing as "transfer resistance."

In a recent article¹⁰ on overvoltages, M. Knobel described data obtained by the commutator method, which would lead to conclusions in support of the above.

DISCUSSION.

WM. BLUM¹¹: At the Ithaca meeting of the American Chemical Society, in September, 1924, Dr. H. D. Holler, of the Bureau of Standards, presented a paper entitled "A Method of Studying Electrode Potentials and Polarization." This paper has recently appeared as Bureau of Standards Scientific Paper No. 504.

Dr. Holler described a method by which a record of the potential of an electrode is produced by an oscillograph, operated by a resistance coupled electron-tube amplifier. In this method no current is taken from the electrode under investigation. It is possible from the oscillograph curves, obtained when the switch for the electrolyzing current is opened and closed, to determine whether any part of the observed potential is due to resistance, as the presence of any resistance causes a sudden change in the potential when the circuit is broken. By superimposing an alternating current upon the cell, it is also possible with the use of the amplifier and a separately excited watt-ammeter to measure the true alternating potential difference due to resistance at the electrode.

The results thus far obtained by Dr. Holler are preliminary. They show clearly, however, that when gas is evolved at an elec-

¹⁰ J. Am. Chem. Soc., 46, 2613 (1924).

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trode there may be an appreciable resistance, which often accounts for a considerable part of the apparent electrode potential, measured with a potentiometer when the current is flowing. As little or no resistance was observed when no gas was evolved, for example, with a copper anode or cathode in a copper sulfate solution, the results indicate that the resistance in the former cases is probably due to a film of gas upon the electrode.

While, therefore, this work definitely established the existence of a resistance at electrodes where gas is evolved, it does not justify the use of the term "transfer resistance." Instead, the term "boundary resistance" was suggested by Dr. Holler, which term does not involve any theory as to the exact source or nature of the resistance.

These results of Dr. Holler suggest the desirability of greater study of the dynamic potentials of those electrodes at which no gas is evolved, such as metal electrodes in metal solutions. As only two phases are there involved, the study and interpretation of the results will probably be more simple, and may lead to methods and conclusions that can subsequently be applied to the admittedly more complicated systems involving a gas phase.

LOUIS KAHLENBERG¹²: May I ask Dr. Ferguson if he has used his interesting apparatus with non-aqueous solutions?

A. L. FERGUSON: No, I have not.

LOUIS KAHLENBERG: In view of what Dr. Blum has said, that these effects might possibly be due to small amounts of gases on the electrodes, I would suggest that while you still have your apparatus a few non-aqueous solutions be used, where the chances for the liberation of gases are less than in aqueous solutions.

WM. BLUM: In that case you have to insure that something will happen at the electrodes. In other words, if the gas is not being discharged there, nothing else may happen and you will not have electrolysis.

LOUIS KAHLENBERG: Make the electrodes non-polarizable ones in aqueous solutions, that is all.

A. L. FERGUSON: If our charge and discharge potentials be plotted against time, there is a gradual rise on the charge side and

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fall on the discharge side. The construction of our apparatus was such, however, that we could not obtain values within about 4° of the end of the charge interval, and about 4° of the beginning of the discharge interval. It is possible that there was a vertical drop during the latter 4° . I intend to redesign the apparatus in order to explore this region in the future. It might be mentioned again that the recent results of Tartar and Keyer at the State University of Washington indicate there is no such thing as transfer resistance. Also the recent results of MacInnes and of Knobel.

